

RADIOACTIVE DATING METHODS

They involve using radioactive isotopes of various elements. Of the more than 1,500 currently known nuclides, more than 80% are unstable although most do not occur naturally on Earth because of their very rapid rates of radioactive decay. To date rocks or minerals naturally occurring radioactive isotopes are used which went on existing long after the big bang because of their extremely slow rates of radioactive decay. These include uranium-238, uranium-235, thorium-232, rubidium-87 and potassium-40. Others resulted from natural nuclear reactions and include radiocarbon and tritium.

Whatever the sources, radioactivity is significant as regards geochronology and radioactive dating started once the phenomenon was discovered and uranium and thorium minerals were found to emit radiation. Using it began in an attempt to determine the age of the Earth. Two new elements were identified, polonium and radium, the latter incorporated in the key word “radioactivity”.

Subsequently there has been ever accelerating progress in determining the ages of minerals, rocks, archaeological and historic objects. The procedures are now routine. Relevant techniques are numerous and have expanded to include radiation damage techniques such as electron spin resonance, fission track dating (energy is transferred from charged particles passing through a solid to its atoms and damage trails are left behind which are visible if irradiated solids are examined using an electron microscope with high magnification (x50,000), pleochroic haloes (zones of discoloration surrounding uranium- and thorium-bearing inclusions in minerals showing such radiation damage effects as a result of the interreaction of alpha particles with atoms in the relevant crystal lattices to produce either displacement of the atoms or their electrons from their equilibrium positions) and thermoluminescence (occurs by heating a body and when electrons trapped in crystal defects are released by this heat and the energy manifests as light emissions when the trapped electrons resume their stable ground states).

In the literature, all too often words such as “assuming”, “presuming”, “implying” and “inferring” are used. Also in some cases, there is dubiety about half-lives and radioactive decay constant. For example, lead-204 is normally regarded as stable, but it is thought to be very slightly radioactive with half-life of 10^{27} years. So there is still a lot of work to be done.

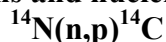
THE RADIOCARBON CLOCK

Many radionuclides are produced in the atmosphere through nuclear reactions involving cosmic rays. They comprise energetic radiation falling on Earth from outer space and contain mostly charged particles such as protons, electrons, etc. About 22% of them are probably made up of heavy atomic nuclei. The proton flux varies according to the numbers of protons emitted by the sun. Similarly with the neutron flux. Cosmic rays originate from the sun and galactic sources. Their flux depends on the kinetic energies of their components which can reach 10^2 GeV ($1\text{GeV} = 10^9$ eV).

Primary particles in cosmic radiation initiate spallation effects when incident atoms of oxygen,

nitrogen and argon are bombarded with high energy protons and secondary neutrons.

Radiocarbon has a half-life of 5730 ± 40 years and it is produced in the atmosphere through the reaction between slow cosmic ray neutrons and nuclei of stable nitrogen-14, thus:



The radiocarbon so produced becomes incorporated into carbon dioxide molecules by reaction with oxygen or by exchange reactions with stable carbon isotopes in molecules of carbon monoxide or carbon dioxide. Radiocarbon decays through the emission of a weak beta particle (or electron) to produce stable ^{14}N .

The rapidity of dispersal of radiocarbon into the atmosphere is demonstrated by measurements of radioactive carbon produced from thermonuclear bomb testing.

Radiocarbon enters the Earth's oceans in an atmospheric exchange and as dissolved carbonate (the entire radiocarbon inventory is termed the carbon exchange reservoir. Plants and animals which use carbon in biological food chains take up radiocarbon during their lifetimes. They exist in equilibrium with the radiocarbon concentration of the atmosphere, i.e. the numbers of carbon-14 atoms and non-radioactive carbon atoms stay about the same over time. As soon as a plant or animal dies, they cease the metabolic function of carbon uptake. Thus there is no replenishment of radioactive carbon, only decay.



where Q is the end point energy, (0.156 MeV). Decay of radiocarbon occurs directly to the ground state with no gamma emission. This decay was first measured by W.F. Libby, T.F. Anderson and J.R. Arnold in 1949 and they determined the half-life as 5568 ± 30 years. This is known as the Libby half-life. From this they inferred that after 10 half-lives, there is a small amount of radiocarbon present in a sample. At some 50-60,000 years, the limit of the technique is reached.

The half-life has been corrected to 5730 ± 40 years. By measuring the carbon-14 concentration or residual radioactivity of a sample of unknown age, it is possible to obtain the count rate (number of decay events) per gram of carbon. By comparing this with modern levels of activity (1890 wood corrected for decay to 1950 AD) and using the corrected half-life it is possible to calculate a date for the death of the sample.

As well as the radioactive carbon-14, two other isotopes of the element exist and these are carbon-12 and carbon-13. These three isotopes are present in the following amounts: carbon 12 98.89%, carbon-13 1.11%, carbon-14 0.0000000001%.

Radioactive decay is the basis of the radiocarbon dating clock. Willard F. Libby used a multi-wire counter to measure radiocarbon contents in archaeological artifacts. The first sample he dated was a piece of acacia wood from furniture in Pharaoh Zoser's tomb at Saqqara, Egypt. Twenty grams were analysed and the date determined was 2030 ± 350 years. Arnold and Libby (1949) noted that, despite the fact that the Earth's magnetic field underwent changes during the past 40,000 years, the initial radiocarbon in a set of archaeologically dated samples was compatible with present day values. The technique developed fast and only ten milligrams

of the same sample were dated in 1992 in the new National Ocean Sciences Accelerator mass spectrometry facility at Woods Hole Oceanographic Institution. The date obtained was 4115 ± 34 years. The Oeschger counter is another indispensable tool for measuring the activity of the naturally occurring carbon-14. H. Oeschger, together with F.T. Houtermans (Berne) built the first Radiocarbon Dating Laboratory in Switzerland and was the first to date the “age” of Pacific deep water.

DENDROCHRONOLOGY

This is important in assessing ages of groundwater, timing the movement of recharge and also for finding out how long ago dead plants and animals died. The latter is possible because once death occurs, such plants and animals are no longer absorbing any radiocarbon directly or indirectly. The initial radiocarbon activity of modern plant and animal tissues is constant to a first approximation and the activity of the radioisotope in archaeological materials of known age is measurable with enough precision to give radiocarbon dates agreeing well with their known historical ages. Analysis of old trees facilitated investigation of the secular variation of the radiocarbon content of the atmosphere. Such trees are dateable because they grew annual accretions of woody tissue to the circumferences of their trunks and layers deposited earlier could not absorb radiocarbon from the atmosphere and their radiocarbon decreases through radioactive decay. Such dendrochronological studies can be used up to 11.4 ka dendro B.P.

AQUIFERS

Time of recharge to an aquifer can be important quite separately from velocity of flow and aquifer parameters. Thus, it can clarify whether a given groundwater receives recharge under the present climatic cycle. Also, it can resolve the question whether the relevant groundwater source can be considered seriously for development as a water supply.

Water entering an aquifer may carry with it radioactive atoms, either as components of the water molecule or as dissolved matter. If there is no further source or sink for these radioactive atoms in the aquifer, the radioactivity of the water and of the dissolved matter will decrease with time according to the law of radioactive decay. A significant use of radiocarbon refers to the age of aquifers which is possible because their radiocarbon contents decay. In assessing turnover times, the optimal method may well be to use this approach.

DATING GROUNDWATERS

K.O. Munnich (1957) proposed using the fact that soil-zone carbon dioxide is of biogenic origin resulting from the respiration of plant roots and plant decay. Of course the radiocarbon ultimately derives from the atmosphere, but has undergone decay. Hence that fraction of the original content remaining is a measure of the time elapsed since its removal from the soil zone, i.e. the time since the associated water infiltrated, t , which is given by: $t = 8270 \ln (C_0/C)$,

where t is in years, 8270 is the mean life of radiocarbon and C is the initial concentration of radiocarbon in the sample. Radiocarbon is measured relative to the total carbon concentration in the sample so the origins both of this and the stable carbon present must be examined. Not all the stable carbon is of the same origin as the carbon-14 because infiltrating water containing carbon dioxide dissolved out of soil zone dissolves carbonate minerals in the soil. Water coming from limestones does not contain radiocarbon, therefore water reaching the water table contains dissolved carbon in the form of H_2CO_3 , HCO_3^- and CO_3^{2-} with carbon-14 content lower than that occurring in the soil (biogenic) CO_3^{2-} . Evaluation of the dilution of soil carbon dioxide originally containing 100% of modern carbon-14 with carbon-14-free (“dead”) carbonate so as to estimate the initial radiocarbon concentration in recharge water reaching the water table is among the most difficult problems of radiocarbon assessment of water.

DeVRIES AND SUESS EFFECTS

Mention should be made of the de Vries effect. This is that the radiocarbon content of the atmosphere certainly varied in a systematic manner in the past. It is claimed that the radiocarbon activity around 1500 and 1700 was as much as 2% greater than in the 19th century.

The Suess effect must be mentioned too. Hans Suess found that the activity of 20th century wood is about 2% lower than that of wood from the 19th century due to the introduction of “dead” carbon dioxide into the atmosphere as a consequence of the combustion of fossil fuels after the Industrial Revolution began. It is interesting that a coral record by Druffel and Griffin (1993) did not show it and this coincided with a change in the nature of the El Nino/Southern Oscillation.

SEPARATING BOMB-PRODUCED RADIOCARBON FROM NATURAL RADIOCARBON

This is possible through the correlation between natural radiocarbon and dissolved silica. On a global range, radiocarbon measurements made on samples collected during the Geochemical Ocean Sections Study (GEOSECS) in 1972 to 1978 were analysed for bomb radiocarbon inventory in the ocean. Later measurements made in the Atlantic during Transient Tracers in the Ocean (TTO) in the early 1980s and the South Atlantic Ventilation Experiment (SAVE) in the late 1980s were analysed for temporal variations in bomb radiocarbon inventory. In the northern Pacific, radiocarbon measurements from samples collected in the WOCE (World Ocean Circulation Experiment program) showed that the observed increase in bomb radiocarbon inventory from 1974 to 1991 is consistent with the first order prediction from a box-diffusion ocean model.

Comparison of results between GEOSECS and TTO/SAVE demonstrated that the bomb radiocarbon inventory increased by 36% in the region north of 10°N and by 71% for the region south of 10°S. These data reflect the radiocarbon uptake for the Atlantic between 1973 (GEOSECS) and 1985 (TTO/SAVE). This information is valuable also in terms of providing

constraints for the carbon cycle in the ocean. Results from CGC-91 (WOCE cruise) show that the observed increase in bomb radiocarbon inventory in the northern Pacific is consistent with first order prediction from a box-diffusion ocean model.

DATING ROCK PAINTINGS WITH RADIOCARBON

H.E. Suess and others (1900) devised a new technique. They used a low temperature, low pressure oxygen plasma to oxidise selectively the organic components which can then be analysed using standard carbon-14 methods. Results were obtained from prehistoric paintings at the Altamira, El Castillo and Niaux caves in Spain and also in the French Pyrenees.

ATMOSPHERIC RADIOCARBON IN THE PAST

Variations have occurred because the rate of formation by the (np) reaction depends mostly on the density of the cosmic ray-produced neutron flux which increases with altitude and attains a maximum at between 12,000 and 15,000 metres above the surface of the Earth. Also the flux is greater by a factor of four in the polar regions. Consequently that rate of production of radiocarbon there should mean that living tissues in that region ought to have more radiocarbon in them than those at the equator.

However, it has been shown that specific radiocarbon activity may be independent of location, possibly because of rapid mixing in the upper atmosphere, a process thought to last less than two years. The result of this tends to produce uniformity at the surface of the Earth.

Also, the neutron flux will vary as the intensity of the solar proton flux does, so that the radiocarbon content of the atmosphere doubtless varied with time in conjunction with alternating solar activity. Finally, the cosmic ray flux may be modified by changes in the Earth's magnetic field during the past 40,000 years or so.

FRACTIONATION OF CARBON ISOTOPES IN NATURE

This entails small systematic errors in radiocarbon dates that can be eliminated when the isotopic composition of stable carbon to be dated can be assessed using a mass spectrometer. The value is expressed as $\delta^{13}\text{C}/\text{‰}$. Such fractionation during photosynthesis alters the abundances of the stable isotopes ^{12}C and ^{13}C from those prevailing in the atmosphere and plants usually become enriched in ^{12}C and depleted both in ^{13}C and ^{14}C .

THE TRITIUM CLOCK

Radioactivity is significant in geochronology and radioactive dating began in an attempt to determine the age of the Earth as soon as the phenomenon was discovered and uranium and thorium minerals were found to emit radiation. Two new elements, polonium and radium, were identified and the latter originated the word “radioactivity”. Great advances followed, among them Hans Oeschger’s development of the Oeschger counter which had a lower background than other such instruments. It has become a leading tool for measuring the radioactivity of a variety of naturally occurring radionuclides such as tritium and radiocarbon. It is these two which are especially important, among other uses, in relation to dating groundwaters. Tritium analysis is done in the laboratory through gas proportional counting and mass spectrometric measurement. Water samples are enriched by electrolysis and the volume greatly reduced. The enriched samples are converted to hydrogen over zinc at 400°C, then the hydrogen is passed into counters and mass spectrometer sample bottles.

Tritium, ^3H , is the radioactive isotope of hydrogen and is produced in the atmosphere by the interaction of cosmic-ray produced neutrons with nitrogen, thus: $^{14}\text{N} + n \rightarrow ^3\text{H} + ^{12}\text{C}$. Tritium decays by beta emission, thus: $^3\text{H} \rightarrow \beta \rightarrow ^3\text{He}$ (tritogenic helium). Once formed, tritium is rapidly incorporated into water molecules and resides in the lower stratosphere for one to ten years. Subsequently, these molecules enter the troposphere and rainout of the tritiated water occurs in a time interval of between five and ten days. The tritium content of natural waters is expressed in tritium units, one tritium unit (1 TU) being equal to an abundance of one atom of tritium to 10^{18} atoms of hydrogen.

Tritium enters the oceans through vapour exchange, rain and continental runoff and most often occurs as HTO (proton-tritium-oxygen). Pre-bomb naturally occurring background levels of tritium are estimated as about 0.2 to 0.5 where $1 \text{ TU} = 10^{-28} \text{ (T/H)}$. The bomb tests of the 1950s and particularly the early 1960s increased the atmospheric tritium inventories by at least two orders of magnitude. Mostly, the bomb tritium entered the surface waters of the high northern latitude oceans within a few years causing a tritium maximum in surface waters by 1964. A model by Doney et al 1993 agreed to within $\pm 10\%$ with the water column inventories. The model results showed that starting in the mid-1970s the annual tritium input from the Arctic exceeded that of all the others combined.

Tritium in the environment from this source reached a prominent peak in the northern

hemisphere in 1964, thereafter steadily declining. The radioisotope undergoes beta decay:

$^3\text{H} \rightarrow \beta \rightarrow ^3\text{He}$ with $Q = E_{\text{max}} = 18.6 \text{ keV}$ and the half-life is 12.43 years.

Tritium also results from solar emissions, the operation of nuclear reactors and particle accelerators on Earth with diminishing quantities originating from earlier testing of thermonuclear devices. These latter added “bomb tritium” which almost eliminated natural tritium as a tracer.

However, a new tool arose, the use of the bomb tritium peak as a “dye” which was delivered to natural water systems from the atmosphere on local to global scales. A way around this involves using tritium with its decay product ^3He ($^3\text{He}_{\text{trit}}$).

DATING USING TRITIUM AND TRITIOGENIC HELIUM-3

To compensate for the decline of bomb tritium input into the environment and continue to use tritium as a dating tool for water in aquifers, rivers, springs, etc., the following approach is used. Simultaneous measurement of tritium and tritogenic helium-3 permits identification of the tritium peak as the sum of helium-3 and tritogenic helium-3 even if most of the tritium has decayed. This also allows direct calculation of age from the radioactivity of mother per quantity of daughter ratio (tritium/helium-3 age).

Determination of the tritium/³He age of groundwater is straightforward.

$$t = \frac{T_{1/2}}{\ln 2} \ln \left(1 + \frac{[{}^3\text{He}_{\text{trit}}]}{[{}^3\text{H}]} \right)$$

The major difficulty in determining the tritium/³He age is the separating of the ³He_{trit} from the total ³He dissolved in a groundwater.

The total helium-3 concentration (³He_{tot}) has a number of sources, namely [³He_{tot}] = [³He_{eq}] + [³He_{exc}] + [³He_{terr}], where ³He_{eq} is the helium-3 in solubility in equilibrium with the atmosphere, ³He_{exc} is helium-3 due to excess air, ³He_{terr} is terrigenous helium-3 (nucleogenic tritium-3 plus mantle helium-3).

Only total helium-3 and helium-3 in solubility equilibrium with the atmosphere can be determined by measurement. If present in a sample, ³He_{exc} and ³He_{terr} must be assessed using measurements of ⁴He and Ne (³He_{terr}).

The total helium-4 concentration measured in a groundwater sample can be presented thus: [⁴He_{tot}] = [⁴He_{eq}] + [⁴He_{exc}] + [⁴He_{terr}], where [⁴He_{eq}] is the helium-4 concentration in equilibrium with the atmosphere, [⁴He_{exc}] is due to excess air and [⁴He_{terr}] is terrigenous in origin. ⁴He concentration (radiogenic helium-4 plus mantle helium-4) can be calculated using the following equation: [³He_{trit}] = [⁴He_{tot}] (R_{tot} - R_{atm}) + [⁴He_{eq}] R_{atm}(1-α), R_{tot} = measured [³He/⁴He] ratio of the sample, R_{atm} = [³He/⁴He] ratio of air (1.384 X 10⁶) and α is the solubility isotope effect. The conversion factor k by which one has to multiply the above [³He_{trit}] value in order to switch from cm³ STP g⁻¹ to TU is given by:

$$k = \frac{4.021 \times 10^{14} \text{ TU}}{1 - S/1000 \text{ cm}^3 \text{STP g}^{-1}}$$

where s is the salinity in ‰. To separate terrigenous He, neon measurements are used.

For separation of terrigenous helium, neon measurements have to be made.

There are two assumptions.

1. the neon comes from only from the atmosphere
2. terrigenic helium-4 equals total helium-4 minus total neon, minus neon in equilibrium with the atmosphere, (helium-4 atm/neon atm) – helium-4_{eq}.

The neon concentration in the sample is measured, the helium-3/neon-atm is the atmospheric He/Ne ratio (0.288) and there is also the neon concentration arising from excess air.

Helium-3 is calculated by multiplying the calculated helium-4 terrigenous (siliclastic sediment deposited or formed on land) value by the helium-3/helium-4 ratio of the terrigenic helium component which can be radiogenic helium, mantle helium or a mixture of both. The best approach to determining R_{terr} is to measure it in groundwater samples from the same aquifer that are free of tritium. If there is no tritium-free groundwater in the aquifer, an estimate can be usually obtained by plotting helium-3 versus helium-4, such a plot offering good clues as to the origin of the terrigenic helium.

The concentration of the atmospheric $^3\text{He}_{atm}$ component is expressed by :

$$[^3\text{He}_{atm}] = R_{atm} ([^4\text{He}_{tot}] - [^4\text{He}_{terr}] - [^4\text{He}_{eq}](1 - \alpha))$$

Other suitable equations are available to facilitate attaining the concentration of $^3\text{He}_{trit}$. Observations have been made on the non-linearity of the tritium/ ^3He age. This age, calculated from the first equation in this presentation, is apparently independent of the initial tritium concentration of the water sample, this being an advantage because it removes the need to establish the precise time-dependent tritium delivery to the aquifer. Of course there is always the possibility that mixing and dispersive factors may affect the tritium/ ^3He age because this is typically biased towards the age of the water component with the higher tritium concentration. For quantitative studies, it is usual to rule out mixing as a significant influence or try to account for it in the final evaluation of the relevant data.

A Danubian application of the tritium/ ^3He dating method came from using tritium, helium-3 and neon concentrations from a shallow groundwater system being recharged by bank infiltration from the Danube in the Szigetköz area of north-west Hungary. The tritium/helium-3 ages increased linearly along the flow lines of as a function of distance from the river. For the deeper groundwater (50 to 100 metres below the surface), which is unaffected by recharge from local precipitation, a horizontal flow velocity of about 500 metres annually was derived from the age gradient. Variation tritium plus helium-3 (“initial tritium”) groundwater data as a function of the tritium, helium age is consistent with the time series of tritium measurements in the Danube for the past 3 years. This confirmed the reliability of the derived residence times. Deviations between the measured Danubian tritium data and tritium and helium data from the aquifer are explicable as a result of dispersive movement and also by interaction with local surficial recharge,

THE CHLORINE CLOCK

Chlorine-36 is produced in the atmosphere through the nuclear reaction $^{36}\text{Ar}(n,p)^{36}\text{Cl}$. This occurs mostly in the stratosphere and its formation is latitude-dependent because of the effects

of terrestrial magnetism on cosmic ray intensities. Mixing is rapid and its atoms attach to atmospheric aerosols in the sub-micron range. These are progressively removed by precipitation from the lower troposphere. Entry into the troposphere varies seasonally and the fallout rate is greater in middle latitudes than at the poles or equatorially.

Chlorine-36 has a half-life of 3.01×10^5 years. This makes it valuable for dating groundwater, glacial waters, etc. Following thermonuclear tests mainly over oceans, the chlorine-36 bomb peak predated that of tritium by about ten years. The bomb pulse has been used to study the migration of water through the unsaturated zone into groundwater aquifers.

There is also subterranean production of chlorine-36 and the world average chlorine contents of granite and basalt have been cited as c. 50 ppm and 200 ppm, respectively. Sedimentary rocks have variable contents ranging from 10 ppm in sandstones to 20,000 ppm in deep-sea limestones. Rock outcrops are exposed to the cosmic neutron flux so that some chlorine-36 results from neutron captured by chlorine-35, but, below a few metres. It is ineffectual.

Nevertheless some chlorine-36 results from an in situ neutron flux in rock matrices caused by (α, n) reaction triggered by alpha particles from uranium and thorium radioactive decay systems.

THE URANIUM CLOCK IONIUM

Thorium-230 (ionium) is a daughter of uranium-234 and produces radium-226 in the uranium-238 radioactive series. Its half-life is 7.52×10^4 years with a decay constant which is $9.217 \times 10^{-6} \text{ a}^{-1}$. Differences in geochemical properties induce thorium isotopes to separate from uranium in the oceans and this is the basis for adding ionium to date deep-sea sediments.

In oxidising conditions, uranium occurs as the uranyl ion UO_2^{2+} whereas thorium remains tetravalent and is rapidly abstracted from seawater by adsorption on to solid surfaces, also by incorporation into authigenic minerals with uranium concentrating in the aqueous phase. The residence time of uranium in oceans is longer by orders of magnitude than that of thorium, namely c. 0.5 million years compared to about 300 years. Most ionium in seawater is formed right there from dissolved uranium-234, but about a quarter is believed to come from river inputs. Preferential removal of ionium from seawater separates it from its parent and produce an excess of unsupported ionium in the sediment. This causes activity which falls off with time, this assuming that both locally formed and river-derived components are altogether removed from seawater.

IONIUM/PROTACTINIUM

Protactinium is a radioactive element with over 20 isotopes. One is ^{231}Pa , half-life 32,480 years, decay constant of $2.134 \times 10^{-5} \text{ a}^{-1}$. A daughter of thorium-231 in the uranium-235 radioactive decay series, its geochemical properties in oceans are similar to those of thorium in that the isotopes are removed from seawater either by adsorption on mineral grains or by the incorporation into authigenic minerals. So sediments deposited in oceans may contain not just unsupported ^{230}Th , but also unsupported ^{231}Pa . If both are removed from seawater equally efficiently, their activity ratios will change with time in a manner controlled by their decay

constants.

LEAD-210

In the uranium series, a daughter of uranium-238, namely ^{222}Rn , enters the atmosphere and decays through several short-lived daughters to lead-210 with a half-life of 22.3 years. This is removed by precipitation with a residence time of about ten days and later may deposit on snow and ice in glaciers as well as in lakes and on coasts. The activity of unsupported lead-210 diminishes as a function of time at a rate determined by its half-life. Lead-210 can be used to date materials containing it. Since the half-life is short, the dating range is only a few hundred years. The method has been used to measure the rates of deposition in snow in Greenland and Antarctica as well as on Alpine glaciers. Lake sediments from Loch Lomond have also been dated. Excess lead-210 unsupported by uranium-238 occurs in volcanic rocks and arises largely from the radioactive decay of excess radium-226, half-life 1,602 years. A Mount Vesuvius sample showed enrichment in ^{226}Ra and also in ^{210}Pb . Lead-210 activity in volcanic rocks increases because of the radioactive decay of excess radium-226 so that deviations in the $^{210}\text{Pb}/^{238}\text{U}$ activity ratios cannot just be ascribed to elemental fractionation effects in the magma. In the oceans, lead-210 distribution was examined through the GEOSECS Program, especially in the Pacific. A lead-210 deficiency relative to its ancestral radium-226 seemed to increase from oceanic interiors towards continental edges and seafloors where it is more intensively scavenged.

THORIUM-230, URANIUM-234. URANIUM-238

Almost no thorium, but substantial amounts of uranium are found in calcium carbonates deposited in saline lakes and also in the oceans, sometimes reaching 5 pp. There is therefore almost no initial thorium-230 activity in newly deposited carbonates, but, due to the radioactive decay of uranium-234, the activity of thorium-230 increases with time. This facilitates dating corals, for instance those from the three lowest terraces in Barbados which is an island emerging from the sea at a uniform rate. The thorium-230/uranium-234 activity ratios of samples gave dates of 122,000, 103,000 and 82,000 years. These coincide with predicted times of elevated summer radiation at 45°N latitude which was actually mentioned by Milankovich, 1920.

THE URANIUM-234/URANIUM-238 CLOCK

Attainment of secular equilibrium is attained in radioactive decay series starting with uranium-238, uranium-235 and thorium-232 depends on none of the daughters entering or leaving the systems concerned. Once the equilibrium is established, then the decay rates of the daughters in any particular system will be equal to that of the parent, expressible thus : $\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \dots \dots \lambda_n N_n$ where $\lambda_1 N_1$ is the activity of the parent and other terms represent those of the daughters. The production of uranium-234 from its parent uranium-238 proceeds through several stages involving alpha and beta emissions.

The problem is that secular equilibrium does not exist, at least in groundwaters and minerals deposited from them. So uranium-234/uranium-238 does not equal unity, but exceeds it as a

result of uranium-234 enrichment through processes such as the alpha decay of the parent. This damages the crystal lattice and allows the daughter to migrate through microcapillaries in the mineral and oxidise to form uranyl ions which dissolve in water and remove it into an aqueous phase.

Uranium-238 occurs in stable lattice positions. Thorium-234 can be rejected from grain surfaces through recoil caused by alpha emission and then decays to uranium-234 through protactinium-234. Radioactive decay of excess uranium-234 and the growth of its daughter thorium-230 have been used for dating of marine and non-marine carbonates of Pleistocene age.

The geochronometer involves determination of the initial (uranium-234/uranium-238)₀ activity ratio and has been applied to dating the calcium carbonate of biogenic and inorganic origin deposited both in marine and non-marine environments.

URANIUM/THORIUM/LEAD

Once radioactivity was identified in uranium and thorium minerals, it was used to date them. The methods included lead/uranium, lead-alpha, uranium/helium, uranium/thorium, lead and common lead. Turning now to the radioactive decay systems used in dating, attainment of secular equilibrium in those starting with uranium-238, uranium-235 and thorium-232 depends on none of the relevant daughters entering or leaving the systems concerned. Once the equilibrium is established, the decay rates of the daughters in any particular system equal that of the parent. Therefore it is feasible to regard the radioactive decay of the uranium and thorium isotopes in minerals as if it went directly to the respective lead isotopes. This simplifies the equations required to describe the growth of radiogenic lead in uranium- and thorium-bearing minerals. There are 4 naturally occurring lead isotopes and these are lead-204, lead-206, lead-207 and lead-208. Relative abundances are 52.4%, 22.1%, 24.1% and 22.1%. Otherwise lead has a total of 32 isotopes, the rest being radioactive and very short-lived. In fact, lead-204 is very slightly radioactive too, but is regarded as stable because its half-life is believed to be 20^{27} years!

The isotopic composition of lead is determined mass spectrometrically. There is an age equation which in the case of uranium-238 is:

$$t = 1/\lambda_{238} \ln \left[\frac{\frac{^{206}\text{Pb}}{^{204}\text{Pb}}}{\frac{^{206}\text{Pb}}{^{204}\text{Pb}} + \frac{^{206}\text{Pb}}{^{208}\text{U}/^{204}\text{Pb}}} \right]$$

where $^{206}\text{Pb}/^{204}\text{Pb}$ is the initial atomic ratio of lead-206 (the final product of the uranium-238 series) to lead-204 (the non-radiogenic lead isotope). λ_{238} is the decay constant of uranium-238, the primary parent of the series assumed to be in equilibrium with all its radioactive daughters. Similar equations exist for uranium-235 and thorium-232.

COMMON LEAD

Common lead, i.e. lead which long lost any association with decay series occurs in many minerals, e.g. galena (lead sulphide) and cerussite (lead carbonate). Such lead has an atomic weight less than that of lead associated with uranium. This difference is due to the increased presence of radiogenic-derived lead-206 in the latter. Common lead contains isotopes

of the element with mass numbers 204, 206, 207 and 208.

CONCORDIA AND DISCORDIA

The concept of 2 independent geochronometers arose from consideration of the radioactive decay of the naturally occurring uranium radionuclides. Concordia plots allow the interpretation of the geological histories of uranium/lead systems. Models have been developed. The dilatancy model takes into account radiation damage to minerals through the alpha decay of uranium, thorium and their daughters. A second model takes chemical weathering into account.

The famous Holmes/Houtermans model of 1946 assumed that all common lead had an isotopic composition explicable by the addition of radiogenic lead as decay products from uranium-238, uranium-235 and thorium-232 associated with a primeval lead at the time of formation of the Earth. The primeval lead was characterized by the relative isotopic abundances α_w , β_w and γ_w , w being the age of the Earth. It was taken for granted that the chemical milieu indices for a given sample of common lead remained constant from w to a time p , where p is the time elapsed since a given sample of lead became incorporated in a lead mineral to which a model age can be assigned. From the general equation of radioactive decay, it is clear that the lead sample changed its composition solely by the addition of the isotopes lead-206, lead-207 and lead-208 from uranium and thorium with which it was linked in the mother rock during the time interval $w - p$.

MULTISTAGE LEADS

Leads in igneous and metamorphic rocks have isotopic compositions determined by a multistage history in most cases, so they will show past associations with a number of systems having different U/Pb and Th/Pb ratios. Lead may be physically transferred from one system to another – maybe by the formation of magma in the mantle and its later emplacement in the crust of the Earth.

WHOLE ROCK DATING

If such magma involving homogeneous material crystallizes, a rock suite results and this may contain different U/Pb and Th/Pb ratios. Alternately, a volcanic rock assemblage might arise after a high grade regional metamorphic episode and contain lead isotopically homogenized by the event. Either way the lead will have evolved along a set of divergent and curved trajectories corresponding to different values for μ (uranium-238/lead-204). If such growth went on until now without interruption, the leads lie along an isochron if the rocks had the same initial isotopes of lead, formed at the same time and remained closed to uranium, thorium and lead. Recent alterations in the concentrations of these elements is permissible as long as the isotopic composition of the lead is not affected. There is an isochron equation giving a slope from which the age of a rock suite can be determined.

THE POTASSIUM/ARGON CLOCK

Potassium has 18 isotopes of which most are unstable. The naturally occurring unstable one is potassium-40 which undergoes branched radioactive decay to calcium-40 and argon-40. That is why the argon-40 abundance in the atmosphere is orders of magnitude greater than would be expected by comparison with the abundance of the other inert gases. Hence excess argon-40 should and indeed does occur in ancient potassium-bearing minerals. That led to the K/Ar dating method. The interesting factor is the radioactive decay of potassium-40 to stable argon-40 which involves electron capture and it also takes place through positron decay with the emission of γ quanta energy (1.51 MeV). Eleven percent of the potassium-40 decays by electron capture to an excited state of argon-40 that de-excites by emission of a gamma ray. About 0.16% of the decays take a more direct route by electron capture straight to the ground state of argon-40. Positron decay is rare, taking place only about 0.001% of the time with an E_{\max} of 0.49 MeV. It is followed by two annihilation gamma rays with a combined energy of 1.02 MeV.

THE RUBIDIUM/STRONTIUM CLOCK

Rubidium has an ionic radius close enough to that of potassium to enable it to substitute for the latter in all potassium-bearing minerals. It occurs as a dispersed element forming measurable parts of micas, potassium feldspar, some clay minerals and feldspars. Two isotopes occur naturally, rubidium-85 and rubidium-87. rubidium-87 decays by negatron emission to strontium-87 with a half-life of 4.8×10^{10} years.

An age equation has been put forward. Standard chemical and mass spectrometric procedures enable measurement of rubidium and strontium concentrations to be made.